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THERMOCHEMISTRY OF GASEOUS COMPOUNDS OF METALS

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High temperature chemistry	Lutetium oxide	
Mass spectrometry	Molybdenum pentafluoride	

20. ABSTRACT *(Continue on reverse side if necessary and identify by block number)*

Thermochemical studies of a number of inorganic gaseous metal halides and oxides were completed, leading to determination of standard enthalpies and entropies of formation from which standard Gibbs energies of formation can be derived. Other properties determined include bond dissociation energies and ionization potentials. The chemical systems studied during this period were tantalum fluorides (monofluoride through pentafluoride), the thulium fluorides

molybdenum pentafluoride and lutetium monoxide. Derived properties of the tantalum fluorides can be used to show that the sharp decline in the rate of corrosive attack of metallic tantalum by atomic fluorine above 2000 K can be explained on purely thermodynamic grounds. Data for the lanthanide fluorides correlate closely with predictions of the Rittner electrostatic bonding model and begin to define trends in the thermochemical properties of the lanthanide halides, while the results for molybdenum pentafluoride and lutetium monoxide resolve major discrepancies involving these species. The results indicate that F-atom detection by means of a gas-phase chemi-ionization process is possible with samarium and europium, but not thulium.

Abstract

Thermochemical studies of a number of inorganic gaseous metal halides and oxides were completed, leading to determination of standard enthalpies and entropies of formation from which standard Gibbs energies of formation can be derived. Other properties determined include bond dissociation energies and ionization potentials. The chemical systems studied during this period were the tantalum fluorides (monofluoride through pentafluoride), the thulium fluorides (monofluoride through trifluoride), europium and samarium trifluorides, molybdenum pentafluoride and lutetium monoxide. Derived properties of the tantalum fluorides can be used to show that the sharp decline in the rate of corrosive attack of metallic tantalum by atomic fluorine above 2000 K can be explained on purely thermodynamic grounds. Data for the lanthanide fluorides correlate closely with predictions of the Rittner electrostatic bonding model and begin to define trends in the thermochemical properties of the lanthanide halides, while the results for molybdenum pentafluoride and lutetium monoxide resolve major discrepancies involving these species. The results indicate that F-atom detection by means of a gas-phase chemi-ionization process is possible with samarium and europium, but not thulium.

Introduction

The objective of this program is to provide reliable thermochemical data (enthalpies, entropies, and Gibbs energies of formation, bond dissociation energies, ionization energies) for high temperature chemical species of interest in aerospace technological applications. Data of this type are used by the engineer, scientist and designer concerned with the analysis of a variety of processes such as combustion, chemical corrosion, propulsion, and chemically-pumped lasing reactions. Sophisticated computer codes based on both equilibrium and nonequilibrium chemistry have been developed for the parametric analysis of a number of

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such processes, but the lack of basic molecular property data as well as the lack of reliable methodologies for estimating these properties often make the results of these computations highly uncertain and of dubious value.

In this program, we have been concerned primarily with the generation, identification, and thermochemical characterization of technologically relevant gaseous compounds of the metals for which information is missing, incomplete, or conflicting. A secondary goal is the correlation of the results with the predictions of various chemical bonding models so that significantly improved schemes for making molecular property estimates can be developed. The recurring demands for such data always exceed the capabilities of the scientific community for producing new experimental results, so that the development of reliable models for both present and future use is quite important.

During the past year we have investigated the tantalum, molybdenum, europium, samarium, thulium, and iridium fluorides, and also lutetium monoxide. The results are particularly relevant to our understanding of the corrosive attack of refractory solids by fluorine and fluorides, and to the analysis of potential electronic-transition laser systems. Summaries of the results obtained are given below.

Results

A. Tantalum Fluorides

The gaseous tantalum fluoride species TaF_n, with $n = 1$ to 5, were generated under equilibrium conditions by admitting $SF_6(g)$ to a tantalum effusion cell at temperatures in the range 1000 to 2500 K. Mass spectrometry was utilized to establish the species identities and then to study several reaction equilibria. Reaction enthalpies were derived primarily by second-law analysis, from which the bond dissociation

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energies and the standard enthalpies of formation of TaF_5, TaF_4, TaF_3, TaF_2, and TaF were derived. The reactions investigated, their derived enthalpy changes, and the resulting thermochemical data are summarized in Tables I and II. Estimated Thermodynamic functions of the Ta-F species, based on data for the neighboring tungsten fluorides, were found to be quite compatible with the equilibrium data, thereby providing a useful set of functions for evaluating the equilibrium abundances of the various Ta fluorides over wide temperature and pressure ranges.

Calculations of the partial pressures of the Ta-F species in equilibrium with Ta(s) showed that at 1 atm pressure, $TaF_5(g)$ remained the major species up to 2500 K. At 10^{-6} atm, however, TaF_5 was the dominant species only up to about 2000 K, as seen in Figure 1. Above 2000 K, the lower Ta Fluorides became successively more abundant, until at 2500 K, the major Ta species was TaF_2. More significantly, however, the calculations showed that above 2200 K, atomic fluorine became the major gaseous species in the system.

This latter point correlates closely with the data of Nordine[1] on the kinetics of gasification of Ta(s) by F-atoms at pressures of 4×10^{-5} to 6×10^{-6} atm. Between 2000 and 2500 K, the observed gasification of Ta leveled off and then declined sharply, consistent with the appearance of atomic fluorine as the major equilibrium species and with the drop in abundances of the Ta-F species shown in Figure 1. Thus the sharp high temperature fall-off in the F-atom gasification kinetics[1,2] of Pt, Ir, Ta, W, and Mo can be rationalized in terms of the equilibrium thermodynamics, as suggested by the quasi-equilibrium (QE) model of gas-solid reactions,[3] rather than a decreased residence time of adsorbed F-atoms at these temperatures.[2] The kinetic implications are believed to be significant, and could greatly improve our understanding of gas-solid corrosive attack processes.
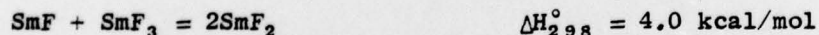
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Of the gaseous fluorides, previous experimental data are available only for TaF_5, the standard enthalpy of formation at 298 K listed as -437.7 ± 1 kcal/mol.[4] This latter value, some 13 kcal/mol more stable than our experimental result, is derived from the enthalpy of formation of TaF_5(s) and a monomer heat of sublimation estimated from vapor pressure data. The comparison, along with subsequent information, indicates the saturated vapor in equilibrium with TaF_5(s) to be highly associated, with an insignificant partial pressure of TaF_5 monomer.

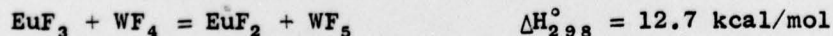This work has been submitted for publication in the Journal of Chemical Physics.

B. Thulium, Samarium, and Europium Fluorides

The gaseous thulium fluorides TmF, TmF_2, and TmF_3 were studied by high temperature mass spectrometry of an effusing molecular beam, using a mixture of TmF_3(s), CaF_2(s), and B(s) as the chemical beam source. Reaction equilibria studied and derived thermochemical data are summarized in Table III. Molecular CaF was used as a reference for derivation of the properties of the Tm-F species. Reactions involving TmF and TmF_2 were studied with both single- and double-chamber beam sources, so that a relatively long temperature range could be covered; all results are based on second-law analyses.

Additionally, the gaseous reactions

$$SmF + SmF_3 = 2SmF_2 \qquad \Delta H_{298}^{\circ} = 4.0 \text{ kcal/mol}$$

and

$$EuF_3 + WF_4 = EuF_2 + WF_5 \qquad \Delta H_{298}^{\circ} = 12.7 \text{ kcal/mol}$$

were studied by mass spectrometry with the second-law results indicated, above, and the data were combined with previous results on the metal mono-fluorides and difluorides to yield complete characterization of the samarium and europium fluorides.

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Derived bond dissociation energies of the Sm, Eu, and Tm fluorides are shown in Table IV. There is considerable variation among the D(M-F) and $D(F_2M-F)$ values, indicating that a model assuming relatively monotonic variation across the lanthanide halide series is inadequate. Indeed, some earlier estimates based on such a model are in error by 15 to 30 kcal/mol. Significantly, however, the Rittner electrostatic bonding model yields values for D(MF) agreeing within 3 kcal/mol with the new experimental results, indicating that the Rittner approach is to be preferred for estimating lanthanide halide properties. The feasibility of extending the Rittner model to polyatomic lanthanide halides is being explored. The low value for $D(F_2Eu-F)$ is consistent with the tendency of $EuF_3(s)$ to undergo partial disproportionation to $EuF_2(s)$ and to vaporize to both $EuF_2(g)$ and $EuF_3(g)$ under neutral conditions, while the high value of $D(F_2Tm-F)$ is compatible with the congruent vaporization of $TmF_3(s)$.

Some of the more volatile lanthanide metals such as the three discussed here are of interest in the development F-atom detectors by means of the chemi-ionization process $M + F \rightarrow MF^+ + e$, similar to that described by Diebold et al.[5] Small concentrations of F-atoms can be detected by mass spectrometric observation of the appearance of the ion product MF^+. This is analogous to the very sensitive chemi-ionization O-atom detector developed by Lawrence and colleagues.[6,7] To be observed, the chemi-ionization process must be exothermic, which implies that $D_0^\circ(MF) > IP(MF)$. Our results show that $D_0^\circ(MF) - IP(MF) = 1.0$, 0.5, and -0.5 eV for SmF, EuF, and TmF, respectively; chemi-ionization is energetically possible for Sm + F and Eu + F at thermal energies, but not for Tm + F. Diebold et al,[5] have observed such chemi-ionization for Sm + F.

C. Lutetium Monoxide

The gaseous equilibrium Lu + YO = LuO + Y was studied over the range 1849 to 1945 K by mass spectrometry, and the dissociation energy of LuO was determined by reference to YO from second- and third-law analyses. A few check measurements with TiO were in agreement, both results leading to the selected value D_0°(LuO) = 158 $\pm$ 2 kcal/mol, some 5-10 kcal/mol lower than other values in the literature. This study is part of a cooperative program with Dr. Edmond Murad, Air Force Geophysics Lab., to look at the systematics of the thermochemistry of the lanthanide monoxides. In particular, the reliability of an excited valence-state model for predicting molecular properties is being evaluated, and the data for LuO provide an essential reference point. At the moment, it appears that the model yields predicted dissociation energies accurate to 5 kcal/mol for the LaO to EuO sub-series, and values that are 10-15 kcal/mol low for the GdO to LuO sub-series. From the lanthanide results to date, it appears that only Eu, Er, Tm, and Yb are energetically forbidden to undergo the gas-phase chemi-ionization process M + O $\rightarrow$ MO$^+$ + e at thermal energies.

D. Molybdenum Pentafluoride

Studies on MoF_5(g) were initiated to resolve a serious discrepancy in the standard heat of formation; recent vaporization studies by Douglas[8] yielded a value some 15 kcal/mol more negative than our previously reported result derived from gaseous equilibrium measurements.[9] We now have completed a new series of thermochemical measurements via the heterogeneous reaction equilibrium

$$5/6\ MoF_6(g)\ +\ 1/6\ Mo(s)\ =\ MoF_5(g) \tag{1}$$
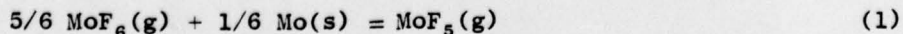
and derived for MoF_5(g) the standard heat of formation -296.6 ± 1.0 kcal/mol, which compares well with our previous value of -296.7 ± 6.8 kcal/mol.[9] The Douglas[8] interpretation of the MoF_5 vaporization data is believed to be in error because of incorrect assumptions about saturated vapor composition. In our judgment, the discrepancy is satisfactorily resolved. The results establish clearly that MoF_4 rather than MoF_5 is the major gaseous species in the high temperature chemistry of the Mo-F system. A manuscript describing the new work on MoF_5 has been accepted for publication in the Journal of Chemical Thermodynamics.

E. Iridium Fluorides

Several attempts were made to investigate reactions of the gaseous iridium fluorides, for which there are no data available in the literature. However, all attempts to observe these species by fluorination of iridium metal in graphite, tungsten, and molybdenum cells were unsuccessful because of preferential attack on the container. Further attempts will be made with iridium-lined cells.

Electron Impact Studies

Because of the extensive electron impact fragmentation of the lanthanide and scandium-group metal trifluoride vapors and the instability of the parent MF_3^+ ions, it is necessary to use the difluoride ion MF_2^+ as a measure of both MF_2 and MF_3 neutrals. This adds several complex features to the interpretation, but the derived results are generally satisfactory. As an alternate approach, we examined the possibility of determining bond strengths and related thermochemical data from electron impact threshold measurements of processes such as
(1) $MF_3 + e \rightarrow MF_2^+ + F + 2e$, and (2) $MF_2 + e \rightarrow MF_2^+ + 2e$, where $D(F_2M-F) \leq \Delta H°(1) - \Delta H°(2)$. Attempts to measure the threshold energy for

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reaction (1) with EuF_3, SmF_3, and TmF_3 were unsuccessful because the presence of small amounts of neutral MF_2 in the MF_3 beams yielded weak tails on the ion yield curves that made it impossible to locate accurately the threshold energy for reaction (1). The weak MF_2^+ parent signals were observed even with platinum effusion cells. Therefore it was necessary to derive thermochemical data for the MF_3 species solely from the equilibrium measurements described above.

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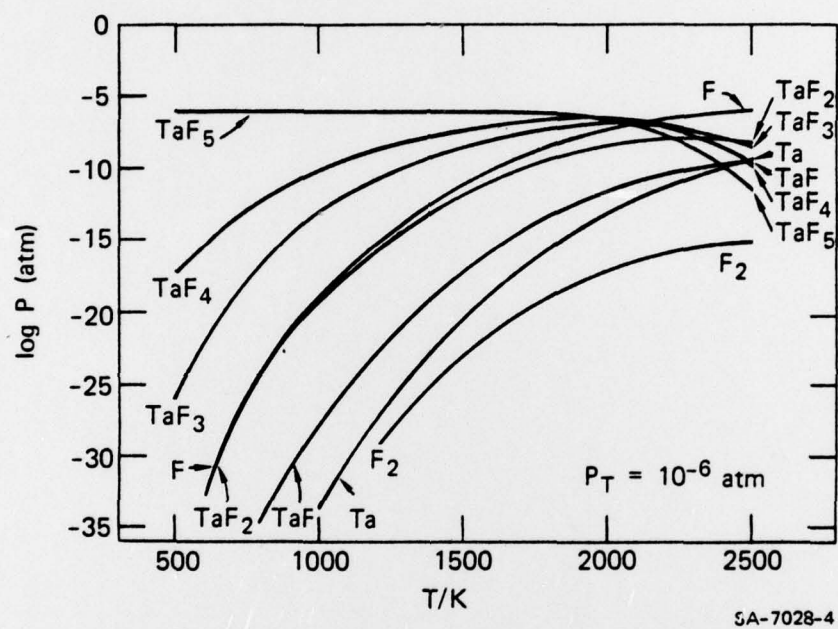
FIGURE 1   EQUILIBRIUM DISTRIBUTION OF GASEOUS SPECIES IN
Ta-F SYSTEM OVER THE RANGE 500 TO 2500 K AT
10^{-6} ATM TOTAL PRESSURE

Table I

THERMOCHEMISTRY OF TA-F REACTIONS

Reaction	Range, K	ΔH_T° (II)[a]	ΔH_{298}° (II)[a]	ΔH_{298}° (III)[a]
(1) $TaF_3(g) + TaF_5(g) = 2\ TaF_4(g)$	1515-1735	8.2 ± 0.6	8.2	10.4
(2) $TaF_2(g) + TaF_4(g) = 2\ TaF_3(g)$	1885-2234	-15.8 ± 0.4	-14.1	-15.7
(3) $TaF(g) + TaF_3(g) = 2\ TaF_2(g)$	2294-2427	-10.6 ± 1.8	-12.6	-10.9
(4) $3/4\ TaF_4(g) + 1/4\ Ta(s) = TaF_3(g)$	1885-2234	32.9 ± 0.7	34.9	32.7
(5) $TaF_4(g) + Ca(g) = TaF_3(g) + CaF(g)$	1770-1929	-	-	3.1

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[a] in kcal/mol

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Table II

DERIVED ENTHALPIES OF FORMATION AND BOND DISSOCIATION ENERGIES

Gaseous Molecule	$\Delta_f H^{\circ}_{298}$ kcal/mol[a]	Bond	D°_{298}, kcal[a]
TaF	69.2	Ta-F	137
TaF$_2$	-68.7	FTa-F	157
TaF$_3$	-194.0	F$_2$Ta-F	144
TaF$_4$	-305.2	F$_3$Ta-F	130
TaF$_5$	-424.6	F$_4$Ta-F	138

[a]Estimated uncertainties in $\Delta_f H^{\circ}_{298}$ and D°_{298} are ±3 kcal/mol.

Table III

REACTION THERMOCHEMISTRY AND DERIVED PROPERTIES OF Tm-F SPECIES

| | | Reaction Thermochemistry | |
| | | ΔH_T° (II) | ΔH_{298}° (II) |
Gaseous Reaction	Range, K	kcal/mol	kcal/mol
Tm + CaF = TmF + Ca	1445-1952	5.3 ± 0.2	5.3
TmF + CaF = TmF$_2$ + Ca	1447-1926	-5.5 ± 0.3	-6.7
TmF + TmF$_3$ = 2TmF$_2$	1445-1564	13.5 ± 2.0	14.6

| Derived Properties | |
Gaseous Molecule	$\Delta_f H_{298}^{\circ}$ kcal/mol
TmF	-47.3
TmF$_2$	-162.1
TmF$_3$	-291.5

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Table IV

BOND DISSOCIATION ENERGIES OF Sm, Eu, AND Tm FLUORIDES

Bond	D_{298}^{o}, kcal		
	Sm	Eu	Tm
(M-F)	135	130	122
(FM-F)	135	131	134
(F_2M-F)	139	119	149